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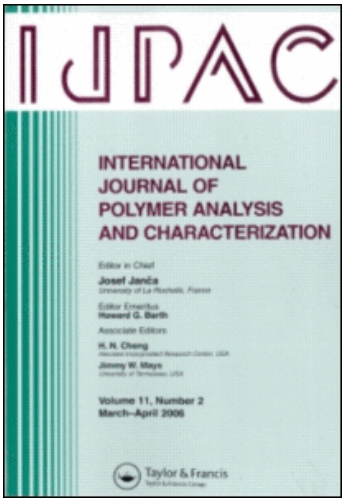

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Composite Particles of Disinfectant Nanocapsules-Skim Rubber Latex

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COMPOSITE PARTICLES OF DISINFECTANT NANOCAPSULES-SKIM RUBBER LATEX

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Skim latex, a by-product of natural rubber latex, was prevulcanized by sulfur and then used in the preparation of composite particles with disinfectant nanocapsules. Each polymeric nanocapsule contained chlorhexidine digluconate (CHD) as a disinfectant agent encapsulated with poly(methyl acrylate) (PMA) as a shell. The driving force for the heterocoagulation of CHD-PMA nanocapsule and sulfur-prevulcanized skim (SPVS) particle was the electrostatic interaction between the positive charge of lecithin residing on the surface of the nanocapsule and the negative charge from the indigenous surfactant (protein-lipid) and/or from sodium dodecyl sulfate on the surface of the SPVS latex particle. The zeta potential and morphology of heterocoagulated particles indicated the formation of the CHD-PMA/SPVS composite particles. Structures and formation mechanisms of the composite particles with different blend ratios were revealed by depth profiling confocal Raman spectra.

Keywords: Composites; Core-shell polymers; Nanoparticle; Rubber; Surfactants

INTRODUCTION

Skim latex, a by-product obtained from the concentrating process of natural rubber (NR) latex, contains small rubber particles (~5% dry rubber content) with high molecular weight of 10^6 g/mol.[1,2] This latex has been used for encapsulating urea fertilizer in a controlled-release application due to the large amount of

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nonrubber substances, including proteins.[3] Similar to the case of NR latex, the prevulcanization or initial cross-linking within the rubber particle is the minimum requirement for skim rubber modification. Drying of the prevulcanized latex produces a cross-linked film without any need of further vulcanization. The physical properties of the final product can be controlled by the design of cross-linking in latex particles.[4,5] A coherent film would be achieved when each latex particle is homogeneously cross-linked. The uniform mesh structure of all sulfur-prevulcanized skim (SPVS) particles observed under transmission electron microscopy (TEM) might also be the reason for the preferred sulfur prevulcanization.[2]

Because of the small particle size (120–200 nm) and homogeneous cross-linked structure, SPVS was previously used as an agglomerating latex in the preparation of composite particles containing NR core (750 nm) by the heterocoagulation process.[2] This technique offers a good possibility for controlling the morphology of composite latex particles, particularly the core-shell type, e.g., polypyrrole/polyacrylic and poly(styrene-co-butadiene)/poly(butyl acrylate).[6,7] The interaction between the core and agglomerating particles is governed by electrostatic, hydrophobic, or hydrogen interactions.[6,8,9] However, the interpolymer complex based on the interaction between poly(ethylene oxide) adsorbed on SPVS particles and indigenous surfactant (protein-lipid) on the NR particle was employed in the preparation of heterocoagulated NR/SPVS.[2] Because of the skim's low glass transition temperature ($-70°C$), the NR/SPVS core-shell particles could be obtained without annealing the composite particles at high temperature.

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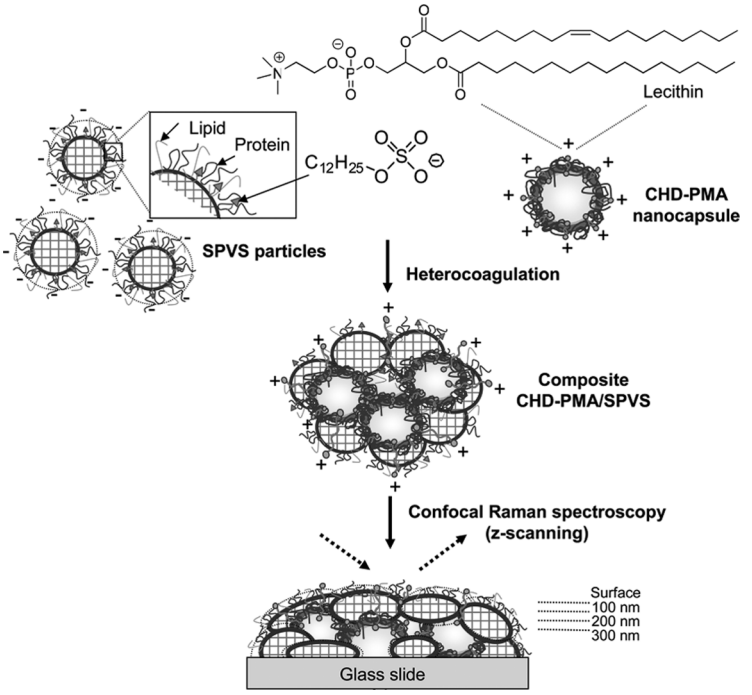

Figure 1. Schematic of the preparation and characterization of composite CHD-PMA/SPVS.

The aim of the present study was to explore potential use of SPVS in entrapment of chlorhexidine digluconate-poly(methyl acrylate) (CHD-PMA) nanocapsules. The SPVS film with good physical properties is expected to be miscible with the substrate when the composite particles are deposited onto a sulfur-prevulcanized NR film for further preparation of disinfectant gloves, desired for minimizing the risk of infection from glove puncture.[10,11] The CHD-PMA/SPVS composite particles were produced by the heterocoagulation technique based on the electrostatic interaction between negative charges derived from indigenous surfactant and SDS on SPVS and cationic charges of lecithin on CHD-PMA nanocapsules. For the first time, structures and formation mechanisms of the composite particles obtained from different CHD-PMA/SPVS blend ratios were characterized by depth profile analysis employing confocal Raman spectroscopy, which is a powerful technique for depth profiling of materials, especially coatings, membranes, and composite materials.[12,13] The overall procedure is schematically presented in Figure 1.

EXPERIMENTAL SECTION

Materials

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Methyl acrylate (Fluka, Purum) monomer was purified by passing through a column packed with neutral and basic aluminium oxide (Fluka, Purum). Sulfur (S; Emco Intertrade Co.), zinc diethyldithiocarbamate (ZDEC; Emco Intertrade Co.), zinc oxide (ZnO; Global Chemical Co.), potassium hydroxide (Merck), sodium dodecyl sulfate (SDS; Fluka), acetone (Lab-scan), hydrochloric acid (Merck), sodium hydroxide (Lab-scan), chlorhexidine digluconate (20% in water, Sigma), potassium persulfate (KPS; Fluka), soybean phosphatidylcholine or lecithin (MP Biochemical), dichloromethane (Lab-scan), cyclohexane (Lab-scan), ethanol (Fluka), methanol (Lab-scan), hexadecane (Fluka), tetrahydrofuran (Lab-scan), and pyrazine (Merck) were used without further purification. Deionized water was used throughout the experiments.

Latex and Characterizations

Total solid content (%TSC) of skim latex (Pan Asia Bio Tech Co., Thailand) was determined using the method described in ASTM D1076:1988. Acetone was used as a rubber coagulant for determination of dry rubber content.[3]

The preparation of SPVS latex and the determination of swelling ratio of latex film were carried out as described elsewhere.[2,14] Vulcanizing ingredients, i.e., S, ZDEC, and ZnO powders, were prepared as 50% aqueous dispersion by ball milling for at least 72 h. The formula used for the preparation of SPVS latex is shown in Table I.

The particle sizes of skim and SPVS lattices were measured by a particle size analyzer (Malvern, Zetasizer Nano ZS). Their zeta potential values were determined using laser Doppler electrophoresis apparatus (Malvern, Zetasizer Nano ZS) at 25°C after adjusting pH by the addition of 0.01 M of HCl or NaOH. Polystyrene latex with known particle size and zeta potential was used as standard for calibration. For the morphological study of skim and SPVS particles, the diluted latex was dried

Table I. Formula used for the preparation of SPVS latex

Ingredients	Parts by wet weight (g)
Skim latex (5.1% DRC)	100
Stabilizers	
−10% w/v KOH solution	4.0
−25% w/v SDS solution	0.8
Vulcanizing ingredients (50% dispersion)	
–S	2.5
–ZDEC	2.0
–ZnO	0.5

on a carbon/copper grid at room temperature before investigating under TEM (JEOL, JEM-2010).

Preparation and Characterization of CHD-PMA Nanocapsules

PMA was synthesized via the mini-emulsion polymerization process as previously described.[15] The average molecular weight ($\overline{M}_w$) of PMA was determined by gel permeation chromatography (Waters/600/2414/600) equipped with refractive index detector.

CHD-PMA nanocapsules were obtained using the modified nanoprecipitation technique.[15,16] PMA (0.15 g) and lecithin (0.1 g) were first dissolved in dichloromethane (12 mL) before the addition of cyclohexane (12 mL), followed by CHD solution (0.5 mL). The mixture was ultrasonicated for 2 min at 90% amplitude (Branson Sonifier, W450 digital) and heated up to 50°C in an open vessel with continuous stirring overnight for the removal of dichloromethane. Cyclohexane was subsequently removed by rotary evaporation at 40°C, and deionized water was finally added to replace the evaporated volume. Size, morphology, and %TSC of CHD-PMA nanocapsules were examined.

For the determination of encapsulation efficiency, the CHD-PMA nanocapsules were separated by centrifugation at 14,000 rpm for 40 min and dried before being dissolved in a mixture of THF and ethanol. D_2O and known concentration of pyrazine were used as a solvent and a calibration standard in the quantitative analysis by ^{1}H-NMR (Bruker, DPX 400). The mass of drug encapsulated in nanocapsules was determined from the area ratio of proton peaks at δ 7.66–9.07 ppm, corresponding to aromatic protons of CHD and pyrazine, respectively.[16]

Preparation and Characterization of CHD-PMA/SPVS Composite Latex

In the preparation of CHD-PMA/SPVS composite latex, a known amount of SPVS latex (1% TSC) was mixed with CHD-PMA nanocapsules (1% TSC, 10 g) with continuous stirring for 10 min at room temperature. The weight ratios of CHD-PMA:SPVS were varied from 1:0.98 to 1:0.06. The zeta potential and morphology of CHD-PMA/SPVS composite latex particles were determined.

Raman spectra of the composite particles at weight ratios of 1:0.98 and 1:0.60, as a function of penetration depth, were recorded on a confocal Raman spectroscope

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(NT-MDT, NTEGRA Spectra). CHD-PMA/SPVS composite latex particles were dropped onto a cover glass and dried at room temperature. Samples were then illuminated with a He-Ne laser at the excitation wavelength of 632.8 nm. Each spectrum was collected at the frequency range 80–5500 cm^{-1} over 60 s with 10 accumulations and a resolution of 2 cm^{-1}. A pinhole diameter of 50 μm was employed. Spectra were recorded at the surface of samples and at various penetration depths with 100 nm intervals.

RESULTS AND DISCUSSION

Characterizations of SPVS Particles and CHD-PMA Nanocapsules

Results from the particle size analyzer indicated that the average sizes of SPVS particles and CHD-PMA nanocapsules in an aqueous phase were 160 and 200 nm, respectively. The morphologies of skim, SPVS particles, and the CHD-PMA nanocapsules under TEM are shown in Figure 2.

The more distinct boundary of SPVS particles in Figure 2(b) compared to the unvulcanized skim particles in Figure 2(a) correlated well with the dense network structure in each SPVS particle.[2] The low swelling ratio of about 200% confirmed full cross-linking of rubber in SPVS latex. The small particle size of skim or the large particle surface area was responsible for the high degree of cross-linking.

For CHD-PMA nanocapsules ($\overline{M}_w$ of PMA = 250 K, encapsulation efficiency = 86%), spherical and well-dispersed nanocapsules with no aggregation were observed in Figure 2(c). The suspension of CHD-PMA nanocapsules in an aqueous medium resulted from the electrical stabilization of lecithin. Zeta potential values of CHD-PMA nanocapsules and SPVS particles at various pHs are presented in Figure 3.

The amphoteric character of skim and SPVS particles with the isoelectric point (pI) at pH 2.8 was observed. The amphotericity is due to the presence of amino acid moieties derived from the native proteins chemically bound to the surface of the skim particles.[14] These particles bore a negative charge at pH above pI. At pH greater than 3 for the skim and 4 for SPVS, the zeta potential values slightly changed, indicating the complete ionization of the ionogenic groupings.[2,17] Since the pI value did not fall into the normal range of protein's pI (4.0–6.0), it was believed that other compounds, e.g., fatty acids and SDS, were present on the skim particle surface.[5]

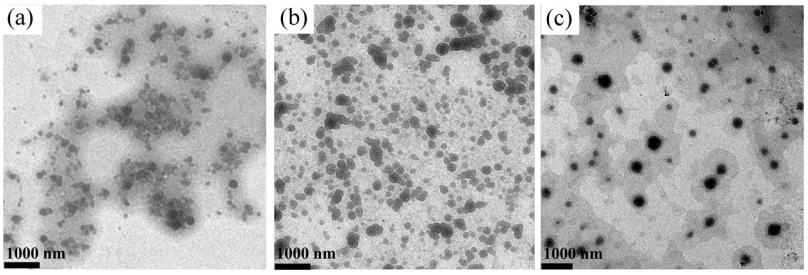

Figure 2. TEM micrographs of (a) skim, (b) SPVS, and (c) CHD-PMA nanocapsules.

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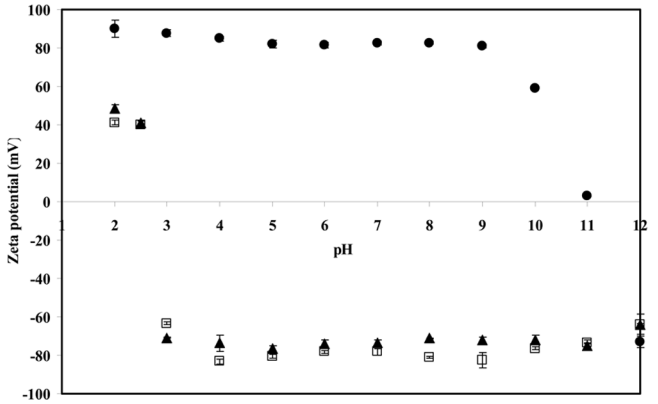

Figure 3. Zeta potential of (●) CHD-PMA nanocapsules, (◆) skim, and (□) SPVS vs. pH.

The results agreed well with the previous work, which reported that the addition of small amounts of carboxylate, sulfonate, and sulfate surfactants whose alkyl chain consisted of approximately 11 carbon atoms effectively enhanced the stability of NR latex by rearranging the indigenous soaps.[18]

For CHD-PMA nanocapsules dispersed in an aqueous medium, the zeta potentials over a range of pH 2 to 10 showed a positive value of 85 mV, derived from the protonation of choline moiety [$N^+(CH_3)_3$] in lecithin.[15] The pI value was shown to be 11 due to the zwitterionic character of lecithin, which contains phospholipids, phosphatidyl, and quaternary ammonium moieties. At pH greater than pI, the zeta potential of CHD-PMA nanocapsules was negative. The current result is in good agreement with the pI value (10.8) obtained from TM-40 silica coated with cationic ATRP macroinitiator possessing choline group.[19]

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Heterocoagulation of CHD-PMA Nanocapsules and SPVS Latex Particles

At pH 4–10, the difference in the zeta potential values of CHD-PMA nanocapsules and SPVS particles reached the maximum point. The high electrostatic interaction between both particles with opposite charges effectively provoked the heterocoagulation. The pH values of the as-prepared nanocapsules and SPVS were selected for mixing both components at various blending ratios. When the blending ratio was not greater than 1:0.2, the aggregates maintained their stability from the incomplete neutralized ionic surfactants and the repulsion from the hydrophobic part of surfactants.[20] To examine the surface charge of aggregates, their zeta potential values at various blending ratios was determined, and the data are shown in Figure 4.

It was believed that the positive value of zeta potentials of composite particles was the result of their surface charges, which were dominated by the $N^+(CH_3)_3$ moiety in lecithin. The assumption was based on the interaction between SDS on the SPVS and lecithin on the nanocapsule. Several studies argued that SDS is more surface active than lecithin and ready to form micelles, which may be trapped inside the lecithin aggregate or bind to the lecithin film. This could be the result of the absorption onto

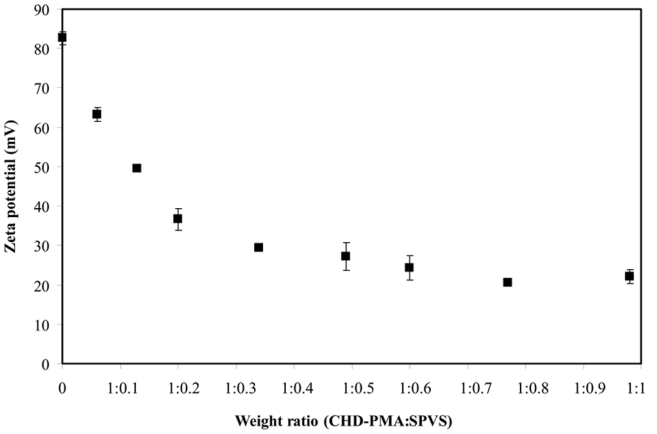

Figure 4. Zeta potential of CHD-PMA/SPVS composite particles prepared with various blending ratios.

the oil droplet surface and the formation of the complex film.[20,21] The SDS-lecithin complex formation may alter the thickness, viscosity, or density of the stabilized layer surrounding CHD-PMA nanocapsules. Although the interaction between SO_4^{2-} and $N^+(CH_3)_3$ may not be strong due to the steric hindrance of lecithin structure, SDS may also cause the lecithin molecule to unfold and change its previous interaction with the PMA or CHD droplet. The binding of SDS onto the surface decreased the electrostatic repulsion between the two components. This explained the fact that zeta potentials of the composite particles significantly decreased from 80 to 30 mV with increase of the weight ratio up to 1:0.3 before reaching to a constant value.

The morphologies of heterocoagulated CHD-PMA/SPVS particles at various blending ratios are shown in Figure 5.

It might be stated that the aggregate consists of CHD-PMA nanocapsules and SPVS particles, as represented in Figure 2 by black and white particles, respectively. Although these particles were similar in size, they were adsorbed in a random manner and formed irregular aggregates of particles.[22,23] This behavior may be due to the simultaneous adhesion of two or three consecutively dissimilar particles by interparticle bridging, which limited the adhesive area on the surface. As a consequence, it saturated more easily than in the regular heterocoagulation. Dispersive Raman spectra of CHD, lecithin, PMA, and CHD-PMA nanocapsules are shown in Figure 6.

All vibrational modes associated with the three components observed in the spectrum of the nanocapsules indicated the presence of these components. Bands due to CHD were observed at 3070, 1600, and 1500 cm^{-1} (ring modes); those of lecithin were located at 1658 (C=C stretching) and 1445 (C–O–C) cm^{-1}. Bands located at 2955 (C–H stretching), 1730 (C=O stretching), and 1454 (C–O–C) cm^{-1} were associated with PMA. The band characteristics of lecithin were very intense despite a low content of the component in the capsules. This confirmed that the molecules were densely located at the surface of the capsules. Figure 6 also shows the spectrum of SPVS, whose characteristic bands were observed at 2932 (C–H stretching), 1665 (C=C stretching), and 1445 (C–O–C) cm^{-1}.[24]

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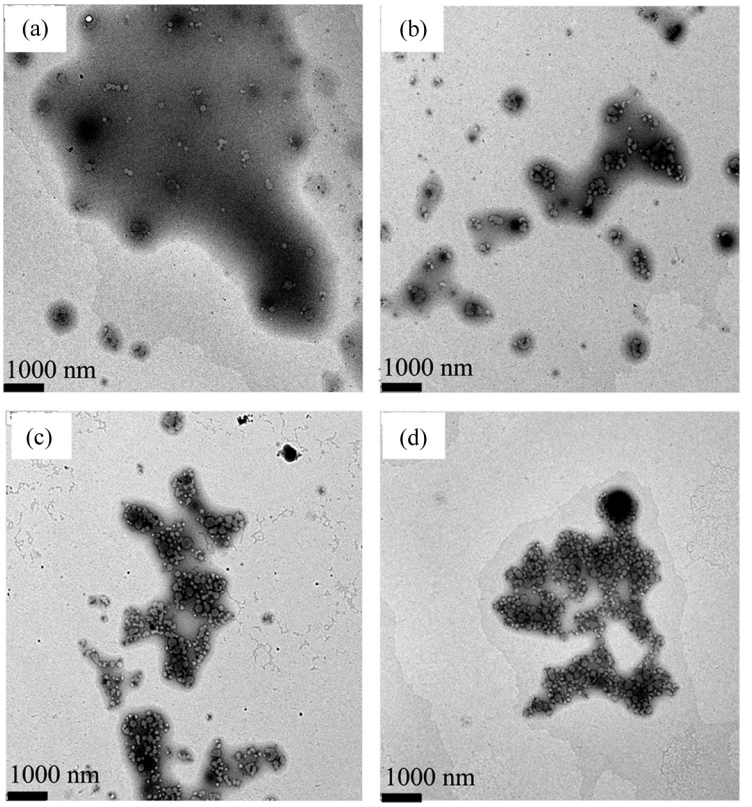

Figure 5. TEM micrographs of CHD-PMA/SPVS composite particles at ratios (a) 1:0.06, (b) 1:0.20 (c) 1:0.60, and (d) 1:0.98.

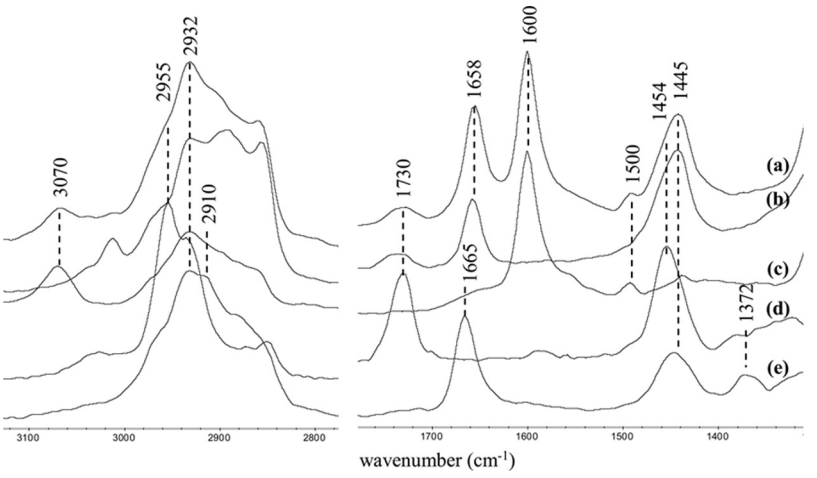

Figure 6. Dispersive Raman spectra of (a) CHD-PMA nanocapsules, (b) lecithin, (c) CHD, (d) PMA, and (e) SPVS.

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Depth profile analysis of the CHD-PMA/SPVS aggregates was studied by confocal Raman using the ''z-scanning'' approach, where the laser was focused on the surface or deeper inside the sample, and the spectrum was recorded at each depth.[25,26] The depth profiling spectra at 100 nm intervals from the surface of CHD-PMA/SPVS composites with a weight ratio of 1:0.98 are shown in Figure 7.

Bands due to SPVS, as denoted by S, were clearly observed from the spectra recorded at the surface and at penetration depths of up to 200 nm. When the laser was focused at 300 nm from the surface, bands due to SPVS disappeared, and those corresponding to PMA and CHD (denoted by P and C, respectively) were clearly observed. This indicated that in the composite with high content of SPVS, the skim present as shell matrix of roughly 200–300 nm thick, encapsulated the CHD-PMA nanocapsules.

On the other hand, the corresponding spectra of the composite with a weight ratio of 1:0.60, as shown in Figure 8, indicate a combination of band characteristics of SPVS, CHD, and PMA at all penetration depths. Significant differences were observed in relative intensities of the bands. As absorbencies of bands are unaffected by penetration depth, the change in band intensities indicates variations in respective functional group contents.[26] This shows that at this blend ratio the relative volume of SPVS to CHD-PMA nanocapsules was not high enough for the skim to form a continuous layer of rubber. The structure of aggregates consisting of random domains of CHD-PMA nanocapsules and SPVS was therefore obtained.

In addition, the depth profiling spectra of the CHD-PMA/SPVS composite particles prepared from both blend ratios clearly showed that the band characteristic of lecithin at 1445 cm^{-1} (denoted by L) is strong at the surface and decreases in intensity as penetration depth increases. This confirmed that the surface of

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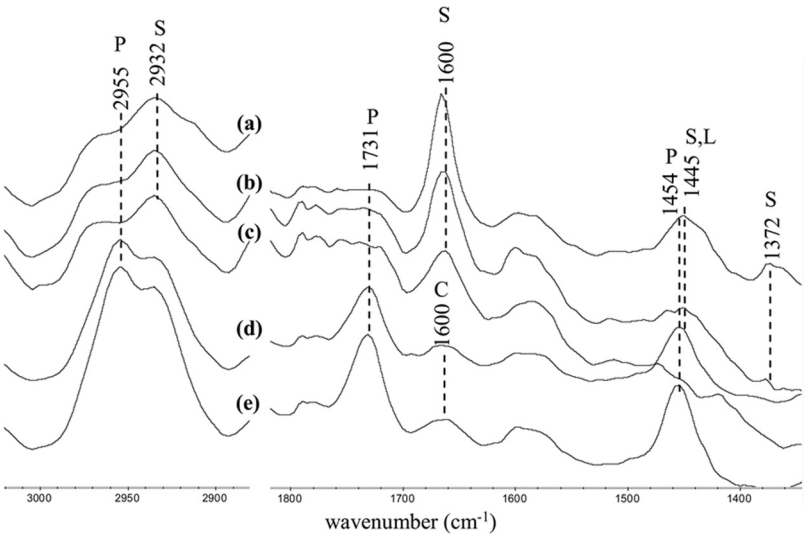

Figure 7. Confocal Raman spectra as a function of penetration depth of CHD-PMA/SPVS composites at a blend ratio of 1:0.98 recorded at: (a) surface, and at penetration depths of (b) 100, (c) 200, (d) 300, and (e) 400 nm. (S, P, C, and L denote band characteristics of SPVS, PMA, CHD, and lecithin, respectively).

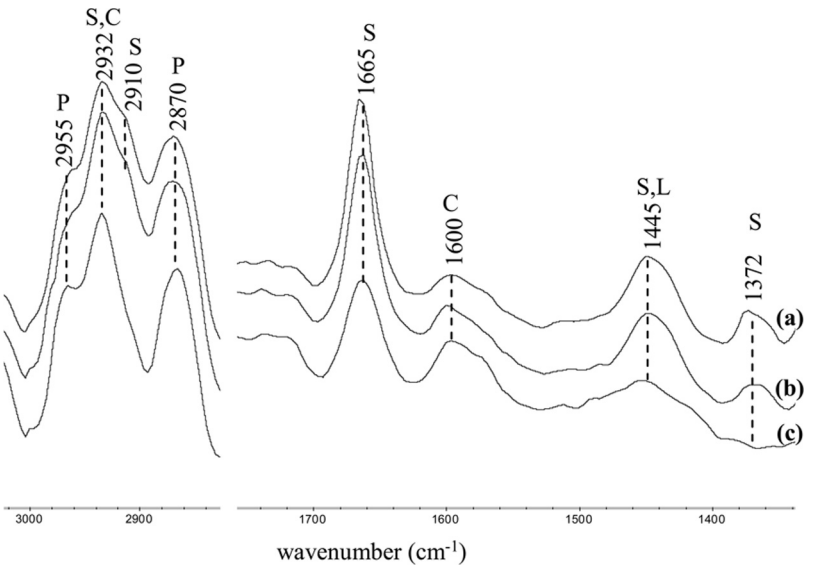

Figure 8. Confocal Raman spectra as a function of penetration depth of CHD-PMA/SPVS composites at a blend ratio of 1:0.60 recorded at: (a) surface, and at penetration depths of (b) 100 and (c) 200 nm. (S, P, C, and L denote band characteristics of SPVS, PMA, CHD, and lecithin, respectively).

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CHD-PMA/SPVS composite particles was dominated by lecithin molecules. The observation is in agreement with that reported by Belaroui et al.[26] in which confocal Raman spectroscopy was employed to observe the migration of sulfate ions to the film/air interface during the formation of dry latex film.

CONCLUSION

CHD-PMA nanocapsules were prepared by the controlled nanoprecipitation of PMA onto inverse mini-emulsion droplets containing CHD. After redispersion of nanocapsules in an aqueous medium, the cationic nanocapsules were heterocoagulated with anionic SPVS latex particles. The size, zeta potential, and morphology of composite particles indicated the aggregation in which the surface charge was dominated by the $N^{+}(CH_3)_3$ moiety in lecithin. Confocal Raman spectra as a function of penetration depth revealed the migration of lecithin to the aggregate surface. The results also indicated that aggregations with different structures were formed, depending on the CHD-PMA/SPVS blend ratios. The corresponding composite particles will be further extended in the preparation of the disinfectant medical glove.

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